Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information

TEMPO-oxidized cellulose nanofibrils; probing the mechanisms of gelation via Small-Angle X-Ray Scattering

Julien Schmitt, Vincenzo Calabrese, Marcelo A. Da Silva, Saskia Lindhoud, Viveka Alfredsson, Janet L. Scott and Karen J. Edler.

Figure S1: TEM micrographs of OCNF at 0.025wt%, stained with uranyl acetate

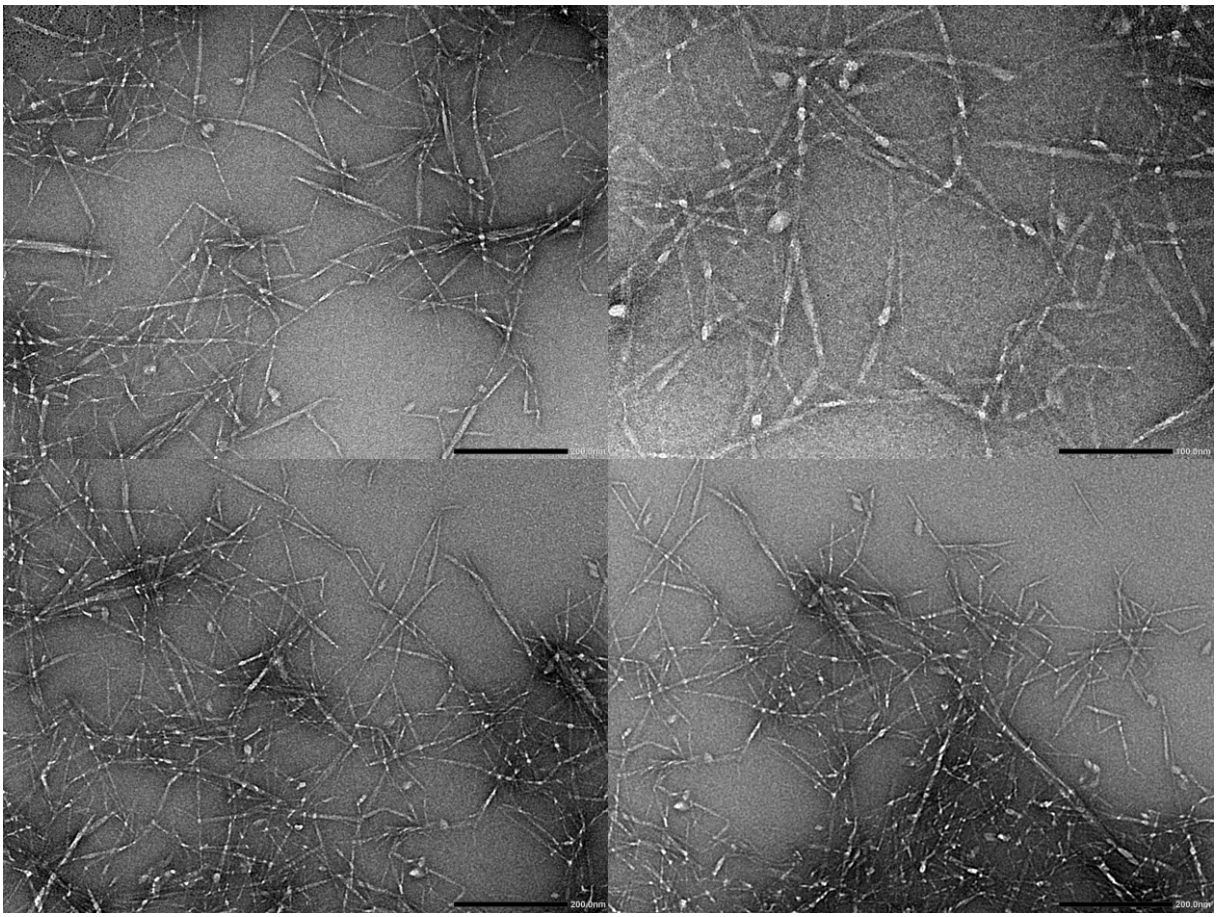
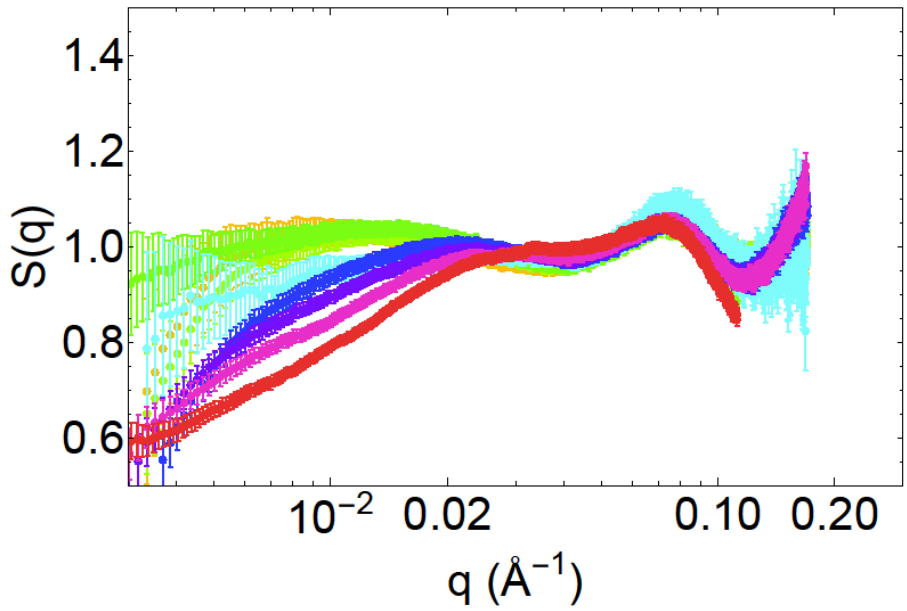


Figure S2: (a) $S(q) = \frac{I(q)}{AF(q)}$ the structure factor obtained by removing the contribution from the form factor to the intensity measured in SAXS and (b) the residuals $(I_{exp}(q) - I_{mod}(q))$ which are the difference on each q vector between the measured intensity $I_{exp}(q)$ and the modelled intensity obtained from the fits $I_{mod}(q)$ for samples at various OCNF concentration: 0.4wt% (yellow), 0.6 wt% (pale green), 0.8 wt% (green), 1wt% (cyan), 1.5 wt% (blue), 2 wt% (violet), 2.5wt% (pink) and 3 wt% (red). The effective structure factor $S(q)$ is proved to diverge strongly from 1 for q< 0.02 $Å^{-1}$ for concentration above 1 wt% due to fibril-fibril interaction. Residuals for the fits are close to zero except below q=0.005 $Å^{-1}$, where the SAXS signal becomes noisy.

a)


1.4
1.2
1.0
0.8
0.6
S(q)
10^{-2}
0.02
0.10
0.20
q (Å^{-1})

b)

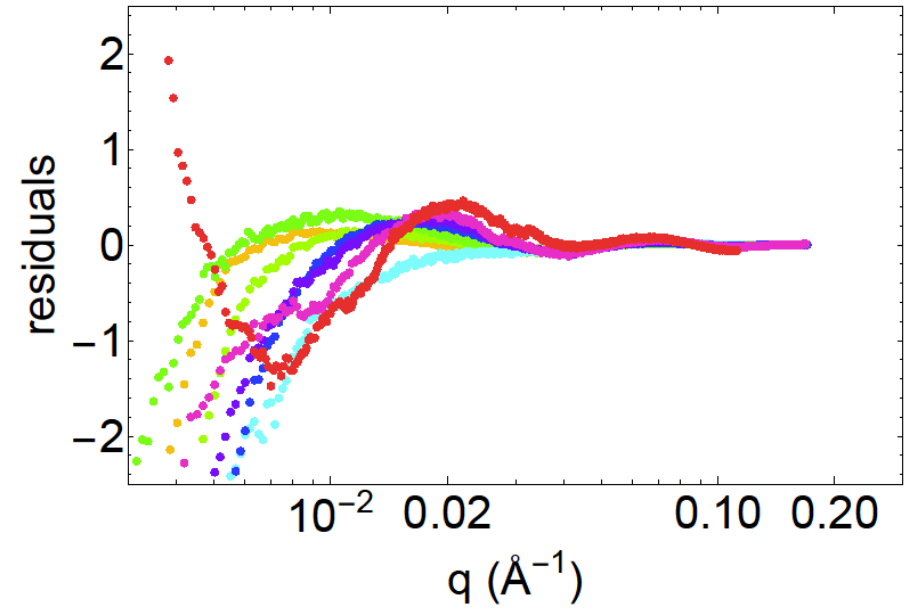
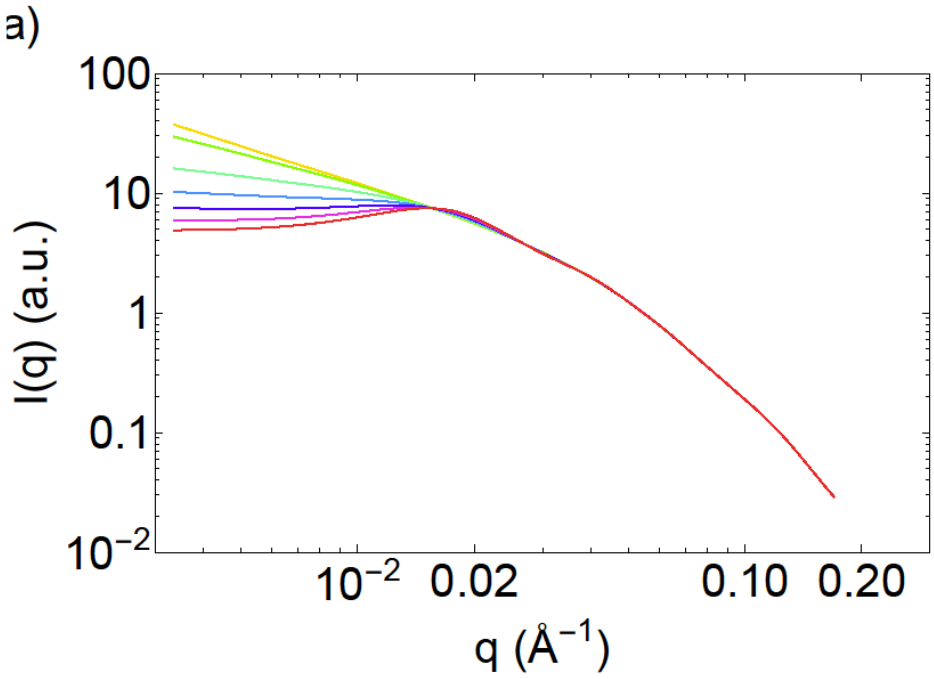

2
1
0
−1
−2
residuals
10^{-2}
0.02
0.10
0.20
q (Å^{-1})

Figure S3: Theoretical SAXS patterns for OCNF nanofibrils with R_{max}=5.1 nm; R_{min}=1.4 nm; L=160 nm and for different structure factor, using the PRISM model with $R_v=3R_{max}$ (a) and $1.5R_{max}$ (b) and v_{RPA}=0 (yellow); 1 (green); 5 (cyan); 10 (blue); 15 (violet); 20 (pink) and 25 (red). It can be observed that for low values of v_{RPA} (<10), R_v has no influence on the pattern. For higher interactions, a correlation peak is observed in the pattern, due to local fibril-fibril excluded volume interaction and phase transition from isotropic to nematic. The position of the correlation peak is strongly related to the value of the local excluded volume R_v as it can be observed by comparing (a) and (b), and its sharpness by both R_v and v_{RPA}. In reality, once local excluded volume interactions are measured via this correlation peak, an increase of concentration will result in a further increase of v_{RPA}, as the global fibril-fibril interaction strength increases, and a decrease of R_v, as the distance between rods decreases.


a)
100
10
1
0.1
10^{-2}
I(q) (a.u.)
10^{-2}
0.02
0.10
0.20
q (Å^{-1})

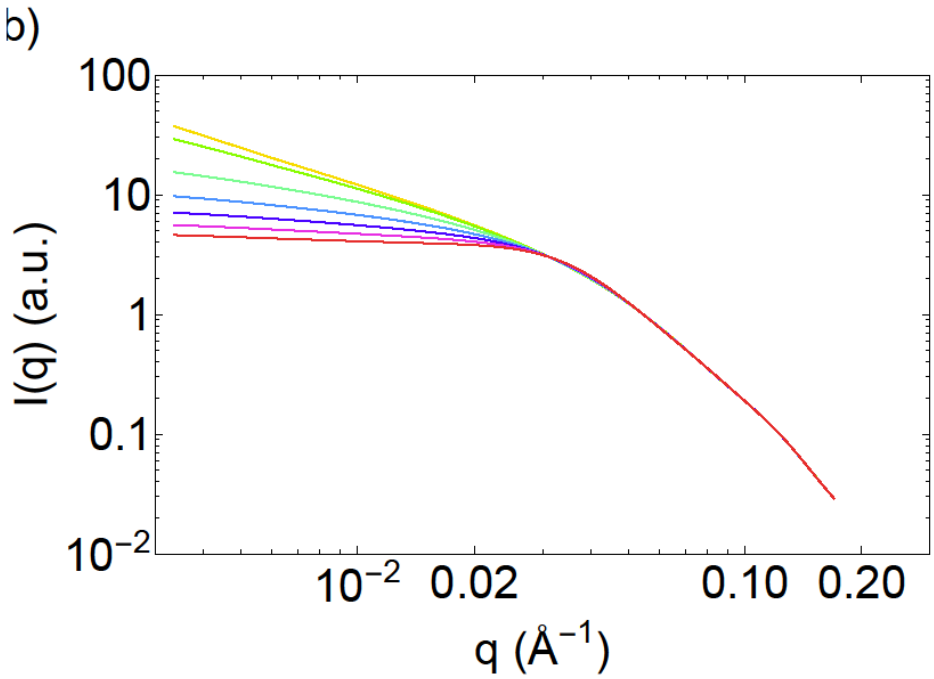

b)
100
10
1
0.1
10^{-2}
I(q) (a.u.)
10^{-2}
0.02
0.10
0.20
q (Å^{-1})

Figure S4: SAXS patterns *I(q)* vs *q* in absolute scaling of OCNF at 1 wt% (green); 2 wt% (blue) and 3 wt% (red), obtained at SOLEIL on a second batch of OCNF dispersions; prepared using the same protocol than described in Material and Methods. Fits, with R_{max}=5.1±0.1 nm and ε=0.27±0.02 and an interaction parameter ν_{RPA}=0 (1 wt%); 1.7±0.2 (2 wt%) and 3.0±0.2 (3 wt%) are given in black dots. Results are completely similar with the first batch studied at Diamond in the main text, proving reproducibility in the samples prepared.

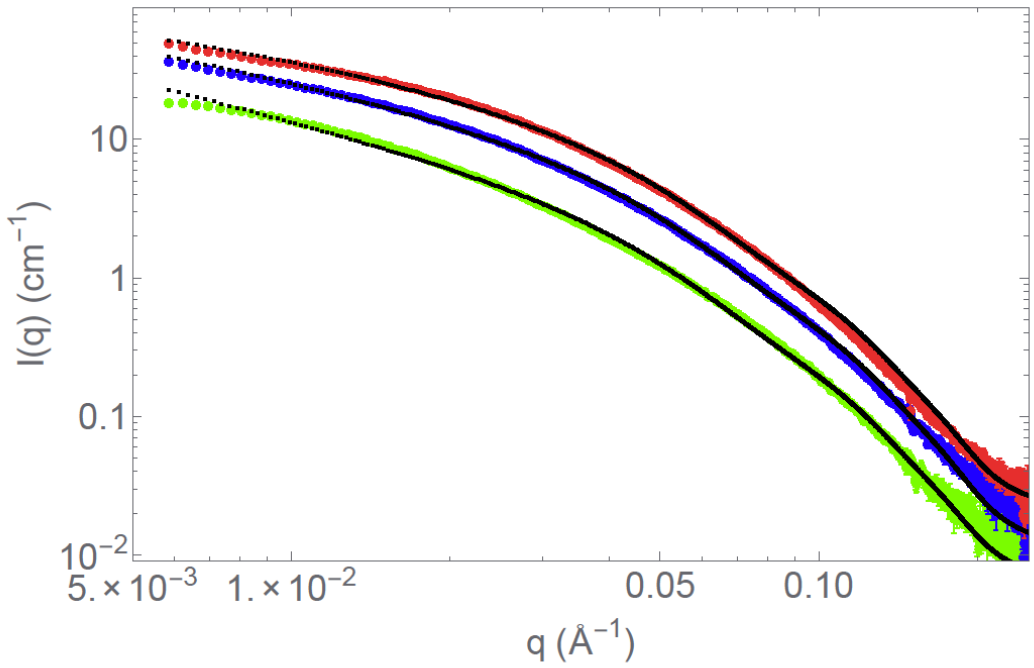
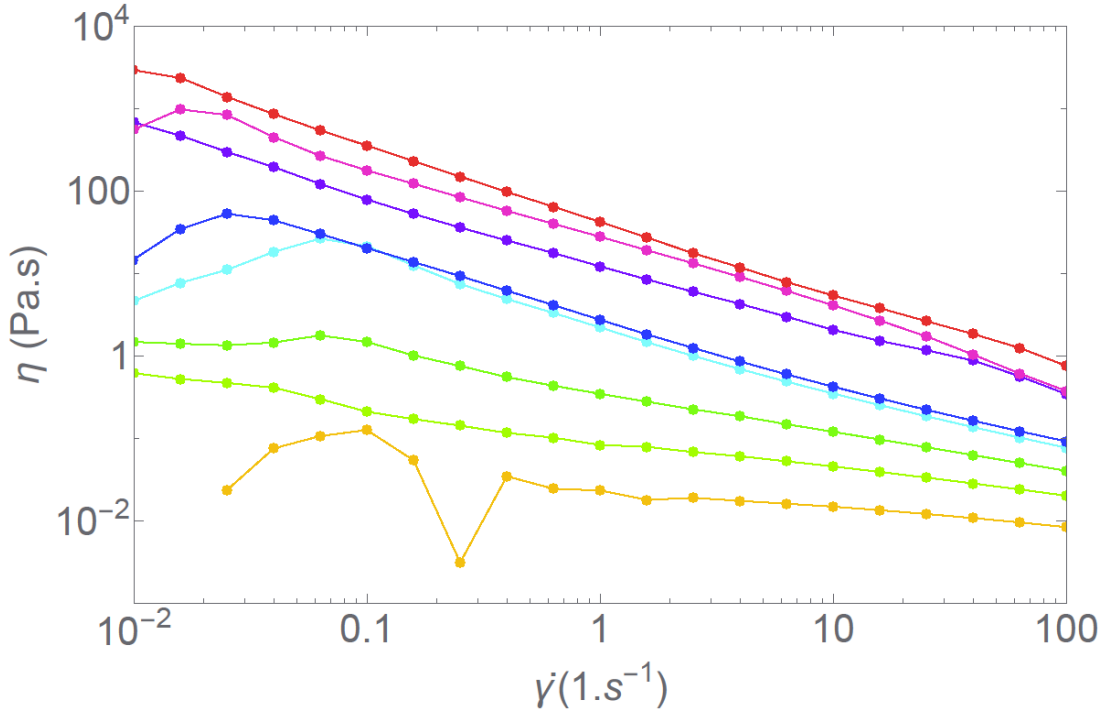
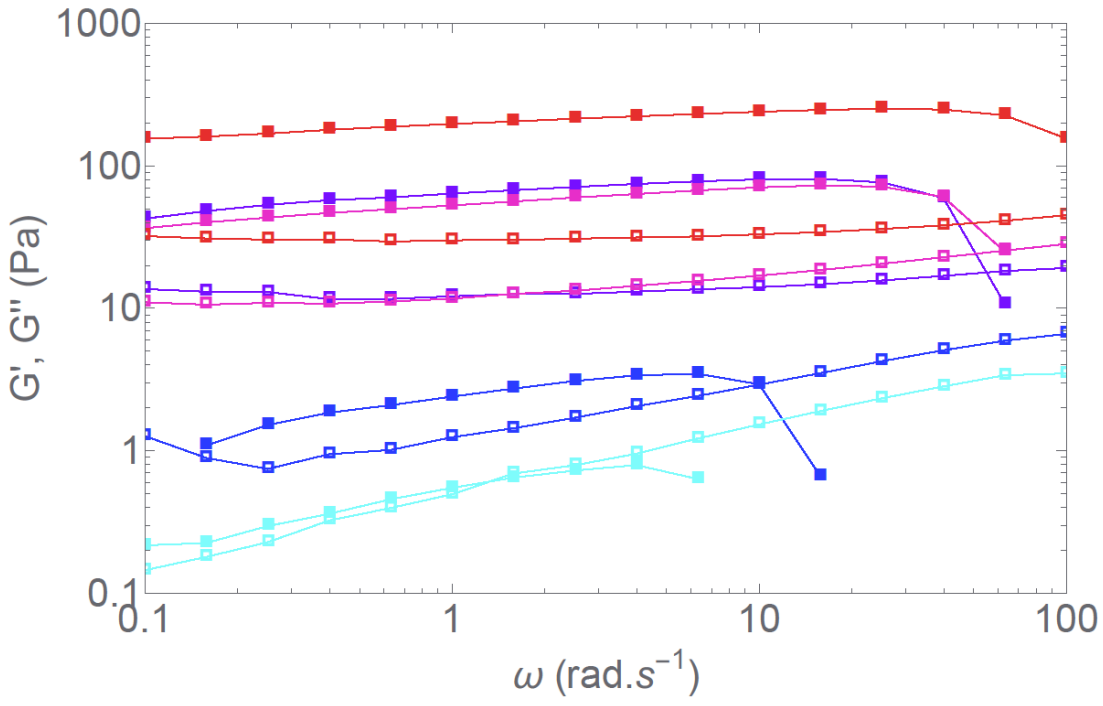


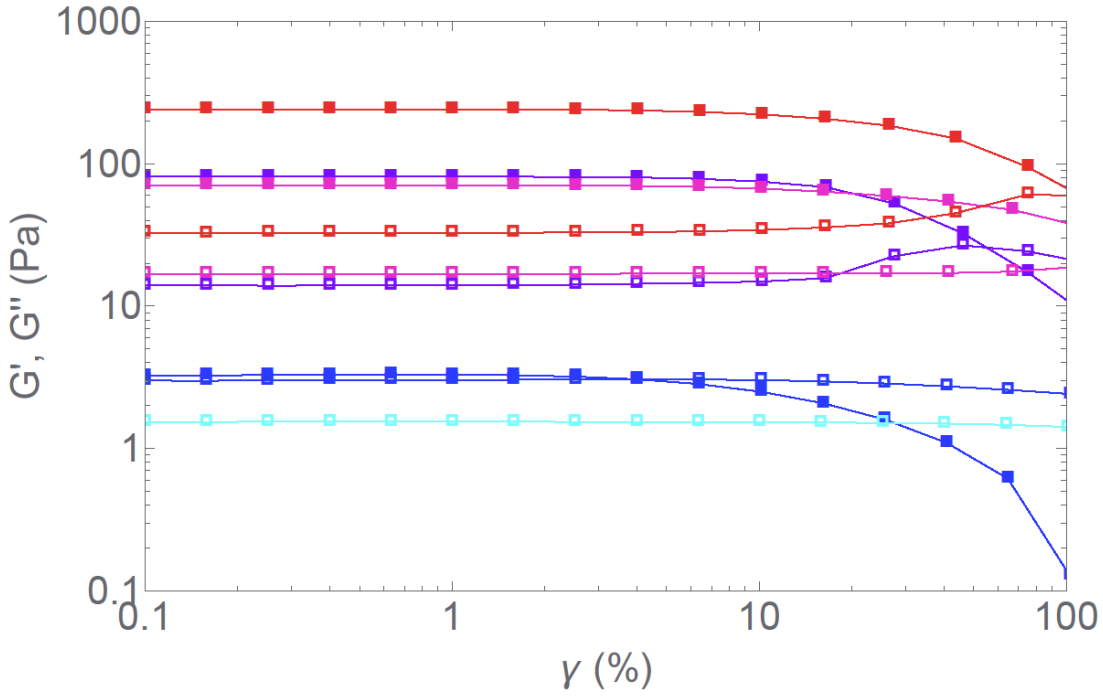
Figure S5: Rheology measurements of OCNF dispersions at various wt% (a) Shear viscosity (b) frequency sweeps and (c) amplitude sweeps at 10 rad/s. OCNF at 0.4 wt% (yellow), 0.6 wt% (pale green), 0.8 wt% (green), 1 wt% (cyan), 1.5 wt% (blue), 2 wt% (violet), 2.5 wt% (pink) and 3 wt% (red). In (b) and (c), solid symbols correspond to G', whereas open symbols correspond to G''.



(a)

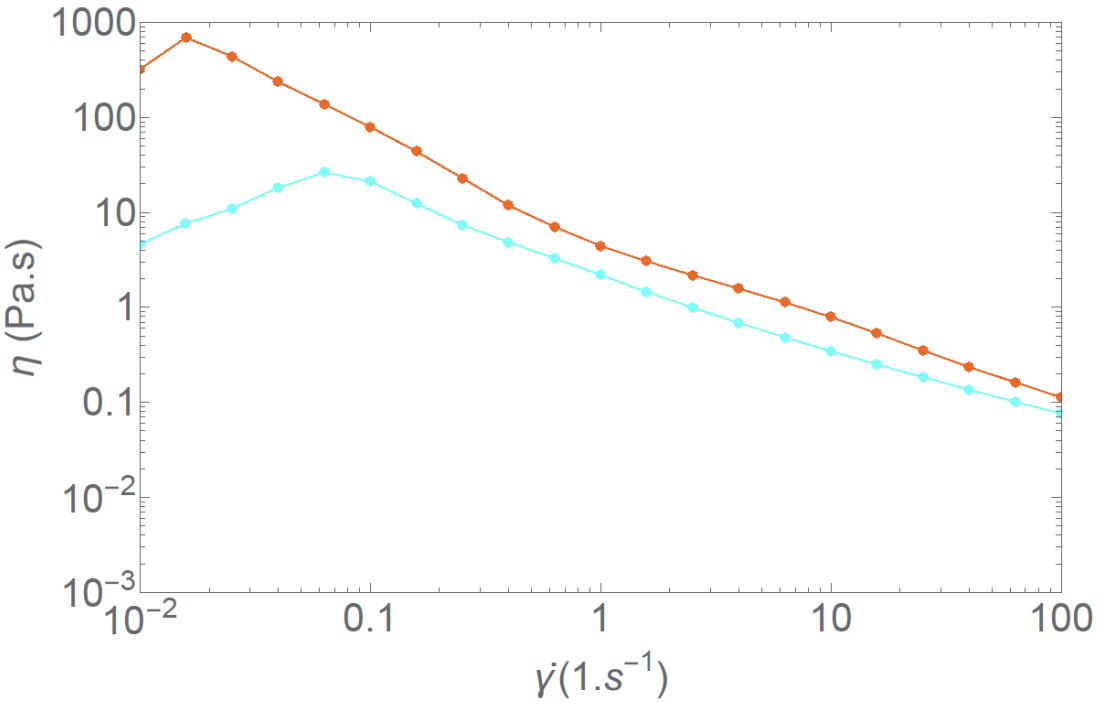


(b)

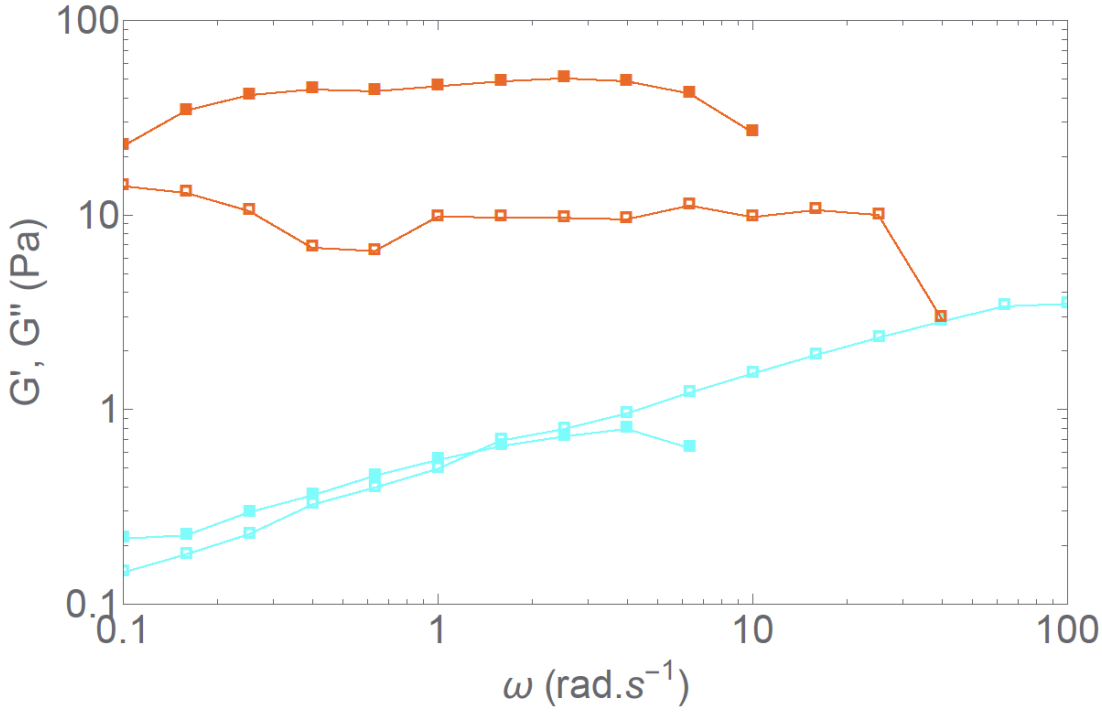


(c)

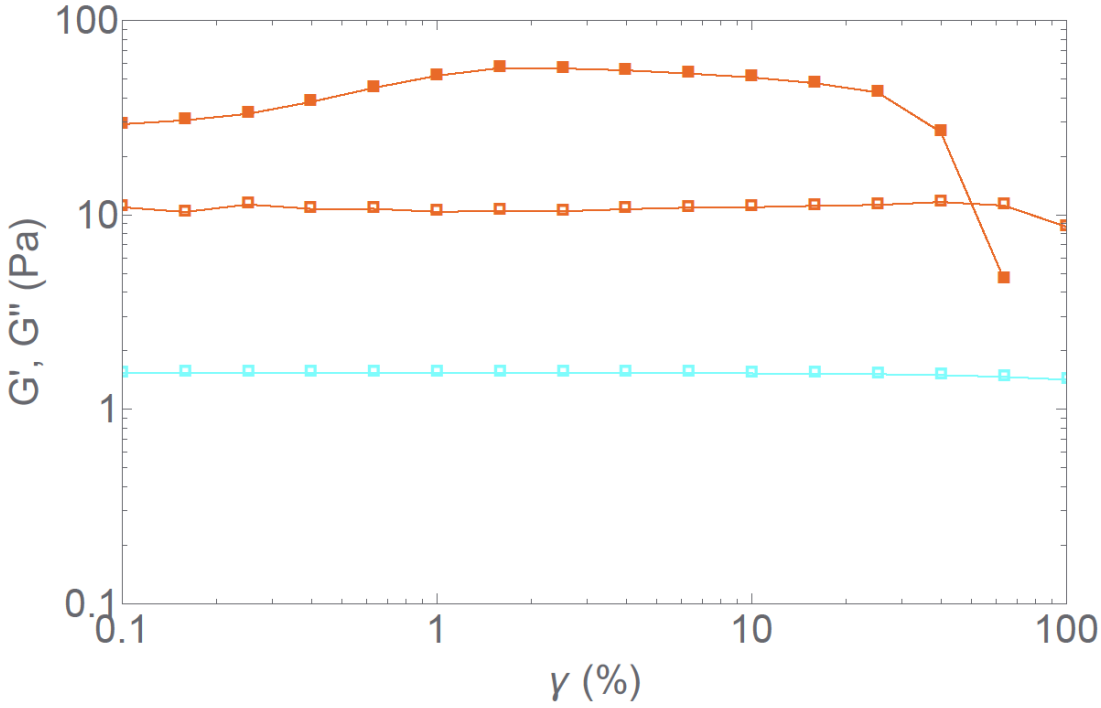
Figure S6: Rheology measurements of OCNF dispersions at 1 wt% (cyan) without salt and (orange) with 0.1 M NaCl (a) Shear viscosity (b) frequency sweeps and (c) amplitude sweeps at 10 rad/s. In (b) and (c), solid symbols correspond to G', whereas open symbols correspond to G''.



(a)

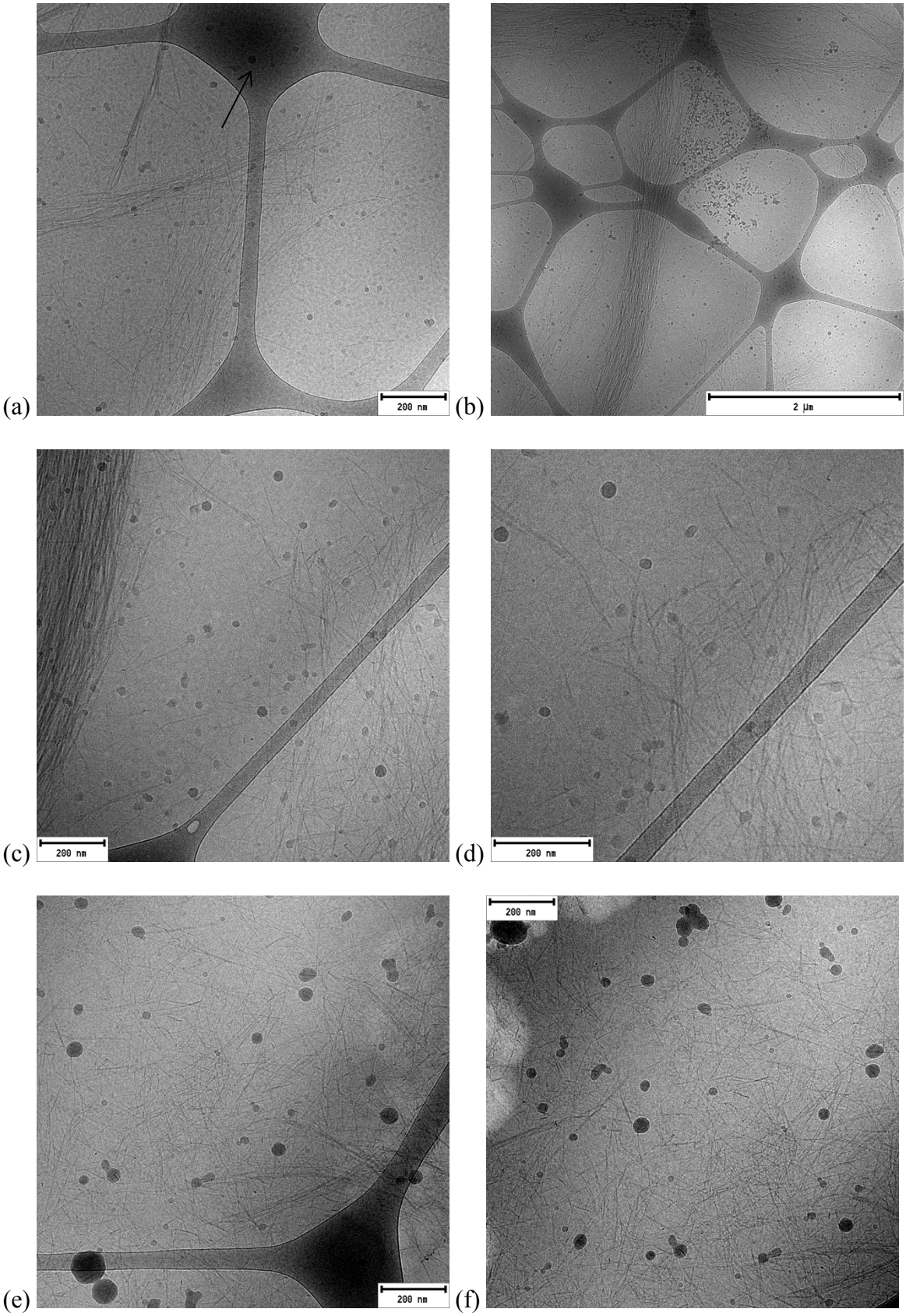


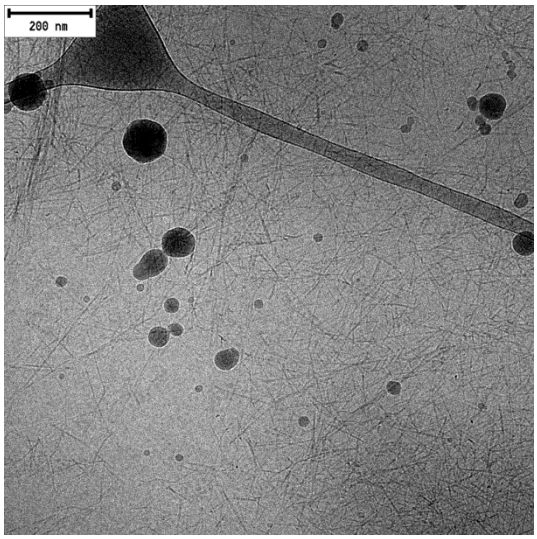
(b)



(c)

Figure S7: Cryo-TEM micrographs of OCNF dispersions at 0.1wt% (a to d) without salt, and (e to h) with 0.1 M NaCl. In the first picture, the black arrow indicates the carbon grid.



(g) 

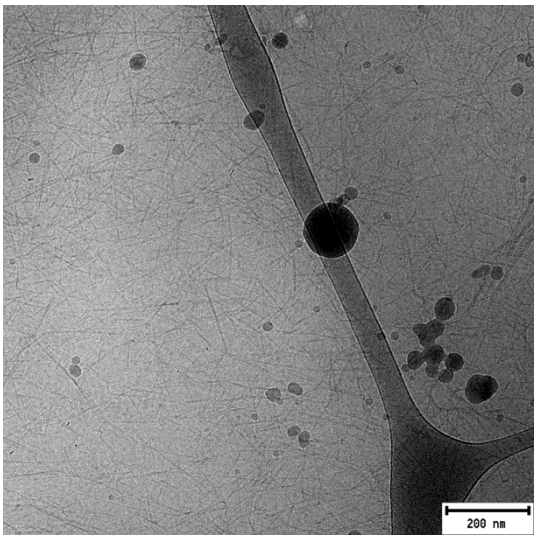
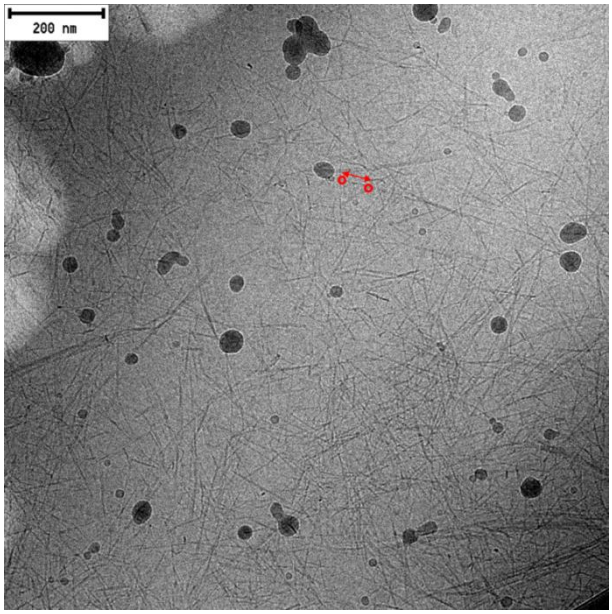
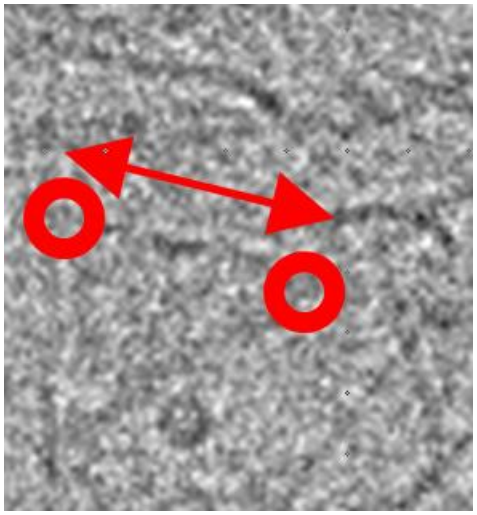
(h) 

Figure S8: Example of the rough estimation of the distance between two contact points between fibrils as observed by cryo-TEM. The sample is OCNF at 1wt%, with 0.1 M of NaCl. Before grid preparation, sample was diluted to 0.1 wt% according to the protocol described in material and methods. (a) cryo-TEM picture with two contact points highlighted by red circles, and the distance between them by an arrow (b), zoom on the area measured and (c) sketch of the same area to highlight the fibrils observed.

(a) 

(b) 

(c)